**Homogeneous Catalysis**

**Boron Lewis Acid-Catalyzed Hydroboration of Alkenes with Pinacolborane: BArF$_3$ Does What B(C$_6$F$_5$)$_3$ Cannot Do!**

Qin Yin, Sebastian Kemper*, Hendrik F. T. Klare,* and Martin Oestreich*[a]

Dedicated to Professor Gerhard Erker on the occasion of his 70th birthday

Abstract: The transition-metal-free hydroboration of various alkenes with pinacolborane (HBpin) initiated by tris[3,5-bis(trifluoromethyl)phenyl]borane (BArF$_3$) is reported. The choice of the boron Lewis acid is crucial as the more prominent boron Lewis acid tris(1,4,7-triazacyclononane)borane (B(C$_5$F$_5$)$_3$) is reluctant to react. Unlike B(C$_5$F$_5$)$_3$, BArF$_3$ is found to engage in substituent redistribution with HBpin, resulting in the formation of ArFBpin and the electron-deficient diboranes [H,BArF]$_2$ and [(ArF)(H)B(μ-H),BArF]. These in situ-generated hydroboranes undergo regioselective hydroboration of styrene derivatives as well as aliphatic alkenes with cis diastereoselectivity. Another ligand metathesis of these adducts with HBpin subsequently affords the corresponding HBpin-derived anti-Markovnikov adducts. The reactive hydroboranes are regenerated in this step, thereby closing the catalytic cycle.

Hydroboration, that is, the (formal) addition of B–H bonds across multiple bonds, finds wide application in synthetic chemistry.[1,2] To overcome reactivity and selectivity issues in these reactions, various transition-metal-catalyzed protocols were developed.[3] However, a practical transition-metal-free approach to alkene hydroboration with simple hydroboranes that employs a Lewis acid as a catalyst is missing although Finke and Moretto had already introduced such a straightforward technique to the related hydrosilylation nearly four decades ago.[4] By replacing AlCl$_3$, which had initially been used as the catalyst for this transformation,[4] with the strong boron Lewis acid B(C$_6$F$_5$)$_3$[5] Gevorgyan and co-workers disclosed a highly efficient alkene hydroboration that proceeds with anti-Markovnikov regioselectivity (Scheme 1 A).[5] Notably, this methodology follows an ionic mechanism, in which the Si–H bond of the hydrosilane is activated by reversible π-coordination to B(C$_6$F$_5$)$_3$, thereby allowing for nucleophilic substitution of the hydride at the silicon atom by the alkene π-nucleophile. The resulting ion pair composed of a β-silicon-stabilized carbamion and a borohydride then undergoes sterically controlled hydride transfer to form the hydrosilylation adduct concomitant with regeneration of the Lewis-acid catalyst. Unlike typical transition-metal-mediated cis-selective hydrosilylations, trans-addition of the Si–H bond across the C–C double bond is obtained.

The analogous hydroboration would require the catalytic generation of the boron electrophile for its reaction with the alkene nucleophile. The feasibility of this strategy is documented by several examples using boreniun ions or equivalents thereof.[6–14] These cationic boron intermediates are typically generated by heterolytic B–H bond cleavage and, in fact, B(C$_6$F$_5$)$_3$ is known to facilitate hydride abstraction from commonly used hydroboranes such as catecholborane (HBcat).[15–17] pinacolborane (HBpin)[18,19] and 9-borabicyclo[3.3.1]nonane (9-BBN).[20] For this, the assistance of a Lewis base (LB) such as a tertiary amine/phosphine or N-heterocyclic carbene is essential, mainly to energetically favor the B–H heterolysis in the neutral tricoordinate hydroborane by coordination and to stabilize the resulting boron cation in the form of its boreniun ion. Due to the increased hydridic character of the B–H bond, the Lewis base adduct of the hydroborane rather than the borohydride [HB(C$_6$F$_5$)$_3$]$^-$ functions as the actual reducing agent in boreniun ion-catalyzed reductions.[11]

We show here that rarely used tris[3,5-bis(trifluoromethyl)]phenylborane (BArF$_3$)[21] enables the catalytic hydroboration of various alkenes with HBpin without the assistance of an external base (Scheme 1 B). Moreover, we reveal that BArF$_3$ (active)

Scheme 1. Boron Lewis acid-catalyzed hydrosilylation (known) and hydroboration (unknown) of alkenes. ArF = 3,5-bis(trifluoromethyl)phenyl.

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[†] NMR spectroscopic measurements.

[**] ArF = 3,5-Bis(trifluoromethyl)phenyl.

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and equally potent B(CF₃)₃ (inactive) behave totally differently in this transformation. This led us to investigate the mechanism of action to explain this striking reactivity difference. The verified reaction pathway also distinguishes itself from those of Lewis acid-catalyzed hydrosilylations[5-7] or hydroborations involving borenium- or boronium-ion catalysis.[9-14]

While parent borane (B₂H₆ as well as BH₃·LB with LB = Me₂S or THF) and dialkylboranes such as 9-BBN are known to readily add across alkenes, boronic esters are usually reluctant to react in the absence of a catalyst even at elevated temperature.[22] We therefore selected HBpin (3) to react with styrene (1a) or oct-1-ene (2a) (Table 1). As expected, treatment of neat 1a with HBpin (3) at 80 °C for prolonged reaction times only showed little conversion (entry 1). We then tested various Lewis acids as potential catalysts for this transformation. As opposed to the related hydrosilylation, AlCl₃ had no effect (entry 2). We then turned toward boron Lewis acids but BCl₃ provided no improvement (entry 3). More electron-deficient B(CF₃)₃, the superior catalyst for Lewis acid-catalyzed hydroboration, provided no improvement (entry 3). More electron-deficient B(CF₃)₃ (inactive) behave totally differently (Table 1, entries 13–16). B(CF₃)₃ did not promote this reaction involving borenium- or boronium-ion catalysis.[9–14]

We then subjected oct-1-ene (2a) as a representative example for an aliphatic alkene to the reaction with HBpin (3) (Table 1, entries 13–16). B(CF₃)₃ did not promote this reaction (entries 13 and 14), while B(CF₃)₃ displayed high catalytic activity, furnishing the anti-Markovnikov adduct 6a with excellent regioselectivity (entries 15 and 16). Isolated yields are higher with α-olefins than with styrenes as polymerization is not competing.

With the optimized protocol in hand, we applied it to differently substituted styrene derivatives (Scheme 2). The new method emerged as widely applicable, and both electron-donating and -withdrawing groups were tolerated on the benzenes ring, furnishing the anti-Markovnikov hydroboration adducts exclusively. Styrenes 1b–d decorated with a methyl substituent at the aryl group were converted with excellent regioselectivities independent of the substitution pattern. However, yields were rather moderate (45–53%) as polymerization was again an issue and became prevalent in the case of 4-methoxystyrene (1e) where only traces of adduct 4e were seen. Conversely, styrenes with an electron-withdrawing group (1f–h) performed significantly better, affording pinacol boronic esters in higher yields (68–71%). Similarly, 2-vinylnaphthalene (1i) underwent smooth reaction in 81% yield. α- and β-Substituted styrene derivatives, for example, 1j, k, and 1m, were also tested successfully. Diminished reactivity was generally observed for these substrates but using two equivalents of HBpin (3) under slightly forcing conditions (80 °C for 40 h) led to improved yields (e.g., 86% for 4k). For unknown reasons, (E)-β-methylstyrene (1l) proved to be unreactive, whereas (E)-stilbene (1m) was cleanly converted into 4m in 87% yield.

We next focused on the substrate scope of aliphatic alkenes (Scheme 3). Hydroboration of α-olefins 2b–g proceeded with excellent anti-Markovnikov regioselectivity (> 94:6). The high isolated yields in the range of 78–92% confirmed that polymerization is not an issue. Notably, allylsilane 2d, allyl silyl ether 2e, and allyl aryl ether 2f underwent clean hydroboration with HBpin (3). An aliphatic bromide substituent as in 2g was tolerated as well. Even 1,1-disubstituted alkene 2h reacted with high efficiency. Our survey also included an internal alkene, and hydroboration of cis-cyclooctene (2i) worked albeit at diminished reaction rate. However, this situation allows the chemoselective hydroboration of a terminal double bond in

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[a] All reactions were performed on a 0.2 mmol scale in a sealed tube. [b] The regioselectivity was determined by GLC analysis. [c] Isolated yield after purification by flash chromatography on silica gel. [d] DABCO (2 mol%) was used as additive. DABCO = 1,4-diazabicyclo(2.2.2)octane.
the presence of an internal double bond, as exemplified with 2j.

To study the diastereoselectivity of the BArF₃-catalyzed hydroboration, we subjected 1-methyl- and 1-phenylcyclohexene 2k and 2l, respectively, to the standard protocol but both did not react (Scheme 4, top). We therefore switched to deuterium-labelled phenylacetylene ([D₁]-8) that cleanly converted into ([E]-[D₁]-9, as verified by NMR spectroscopy (Scheme 4, bottom). This outcome is good evidence in favor of a 1,2-cis-hydroboration and against 1,2-trans- or 1,1-hydroborations.

To understand the reactivity difference between BArF₃ and B(C₆F₅)₃, we performed stoichiometric control experiments (Scheme 5). Monitoring the reaction of BArF₃ with HBpin (3) at elevated temperature by multinuclear NMR spectroscopy in the absence of an alkene revealed that ligand redistribution occurs.[23, 24] For example, treatment of BArF₃ with excess HBpin (4 equiv) in [D₈]toluene at 80 °C for 20 hours resulted in complete consumption of the borane and clean formation of ArFBpin (10) and diborane (B₂H₆, 11) (Scheme 5, top and Figure 1; see the Supporting Information for NMR spectra). The detection of minor amounts of the higher borane B₅H₉ may be ascribed to the decomposition of B₂H₆ at temperatures higher than 50 °C. At room temperature, the redistribution process proceeds slowly, presumably as a consequence of the poor solubility of BArF₃ in toluene. Since B₂H₆ is known to readily undergo addition to C=C multiple bonds, we added styrene (1a) to the reaction mixture and observed that 1a is indeed consumed when heated at 80 °C for 24 hours. However, just traces of the hydroboration adduct 4a were formed in the presence of HBpin (3), hence excluding B₂H₆ as the actual catalyst.[25, 26] To identify the true nature of the catalyst, we studied the reaction of BArF₃ with HBpin (3) with varied stoichiometries. In the ideal case (see the box in Scheme 5), BArF₃ reacts with three equivalents of HBpin (3) to generate three molecules of ArFBpin and one molecule of BH₃ (dimerizing to B₂H₆). However, when BArF₃ was treated with only one or two equivalents of HBpin (3), we observed two new boron compounds, eventually identified as diboranes [H₂BArF]₂ (16) and [(ArF)(H)B(μ-H)₂BArF]₂ (17), respectively (Scheme 5, bottom and Figure 1; see the Supporting Information for NMR spectra). These in situ-formed electron-deficient hydroboranes are expected to be highly reactive hydroboration reagents[27, 28] and were indeed found to instantly add across 1a with high regioselectivity to afford the boranes 18 and 19.[29] Substituent exchange reaction with HBpin (3) at elevated temperature then yielded the final adduct 4a. Analogous control experiments with B(C₆F₅)₃ showed decomposition of HBpin into B₂pin, and several unidentified compounds by Lewis acid-promoted ring opening.[31] Ligand metathesis that would generate the corresponding hy-

**Scheme 2.** Substrate scope I: Hydroboration of styrene derivatives.

**Scheme 3.** Substrate scope II: Hydroboration of aliphatic alkenes. TIPS = triisopropylsilyl.

**Scheme 4.** Probing the diastereoselectivity of the BArF₃-catalyzed hydroboration.
droborane \([\text{H}_2\text{B}(\text{C}_6\text{F}_5)_2]\) or Piers’ borane, \([\text{HB}(\text{C}_6\text{F}_5)_2]\), was not seen (see the Supporting Information for NMR spectra).

Based on literature precedence [27, 28] and consistent with our stoichiometric control experiments, we delineate the following mechanism for the \(\text{BAR}_3^+\)-initiated alkene hydroboration (Scheme 6). Initial substituent redistribution between \(\text{BAR}_3^+\) and \(\text{HBpin}\) presumably through \(\sigma\)-bond metathesis (see 20) leads to the formation of electron-deficient hydroboranes 16, 17, and 21 that instantly undergo concerted 1,2-\(\text{syn}\) addition of the \(\text{B}/\text{C}^0\) bond across the alkene \(\text{C}/\text{C}^0\) double bond of 1a in a highly regioselective manner. While only hydroborane 16 and the mixed dimer 17 were detected in the stoichiometric experiments (cf. Scheme 5), it cannot be ruled out that \([\text{H}_2\text{BAR}_3^+2]\) (21) formed as the initial intermediate is catalytically competent. Another ligand exchange between the resulting hydroboration adducts 18 and 19 with HBpin is likely to be the rate-determining step, eventually furnishing HBpin-derived adduct 4a concomitant with regeneration of the hydroboration reagents. Hence, \(\text{BAR}_3^+\) acts only as a precatalyst and does not participate in the overall catalytic cycle.

![Scheme 6. Catalytic cycle for the \(\text{BAR}_3^+\)-initiated hydroboration with HBpin (shown for styrene as substrate).](image)

Figure 1. Monitoring the reaction of \(\text{BAR}_3^+\) with HBpin by \(^1\text{H}\) NMR spectroscopy (500 MHz, \([\text{D}_8]\)toluene) using different stoichiometries: detection of the key intermediates (scale of the downfield y axis is amplified for clarity).
In conclusion, the boron Lewis acid BArF$_3$ was uncovered as the precatalyst for the 1,2-cis-hydroboration of alkenes with HBpin. B(C$_6$F$_5$)$_3$ cleaves the 1,3,2-dioxaborolane ring of HBpin whereas BArF$_3$ engages in substituent redistribution with HBpin, thereby forming electron-deficient hydroboranes as the actual hydroboration reagents. This unexpected reaction mode constitutes an alternative to the trans-selective hydroboration involving borenium-ion catalysis$^{[10]}$ and avoids the need of added base. Further efforts to expand this methodology are the subject of ongoing investigations in our laboratory.

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Keywords: alkenes · boranes · homogeneous catalysis · hydroboration · Lewis acids

[17] We independently tested BH$_3$·SMe$_2$ as a catalyst (2 mol%) for the hydroboration of styrene with HBpin under neat conditions at 50 °C. However, only 15% conversion of styrene was observed after 14 hours.
[19] Hoshi and co-workers reported the catalytic hydrosilylation of terminal alkenes with HBpin using HBCy$_2$·SMe$_2$ generated in situ by treatment of B(C$_6$F$_5$)$_3$ with BH$_3$·SMe$_2$; a) M. Hoshi, K. Shirakawa, M. Okimoto, Tetrahedron Lett. 2007, 48, 8475 – 8478; for the analogous HBCy$_2$-catalyzed hydroboration, see: b) K. Shirakawa, A. Arase, M. Hoshi, Synthesis 2004, 1814 – 1820.
[20] It must be noted here that independently prepared HBArF$_3$·SMe$_2$ (see Ref. [30]) as well as Piers’ borane, [HB(C$_6$F$_5$)$_2$]$_2$, indeed proved to be active catalysts for the hydroboration of styrene with HBpin under neat conditions at 50 °C.
Boron Lewis Acid-Catalyzed
Hydroboration of Alkenes with
Pinacolborane: BArF₃ Does What
B(C₆F₅)₃ Cannot Do!

Scrambled puzzle: Unlike B(C₆F₅)₃, the
rarely used boron Lewis acid BArF₃
(ArF = 3,5-bis(trifluoromethyl)phenyl) ini-
tiates the catalytic hydroboration of var-
ious alkenes with pinacolborane. No as-
sistance of an external base is required.

An unexpected mechanism accounts for
this striking reactivity difference leading
to a cis-selective hydroboration as op-
posed to typical Lewis acid-catalyzed
hydrometalation reactions.